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## PATENT ABSTRACTS OF JAPAN

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### (54) RESIN COMPOSITION FOR SEALING LIQUID CRYSTAL AND PRODUCTION OF CELL FOR SEALING LIQUID CRYSTAL

(57)Abstract:

**PURPOSE:** To obtain the subject composition, consisting essentially of an epoxy resin, organic acid hydrazides, a rubber, a filler and a solvent, capable of providing a specific value of impurity concentration according to a solvent extraction method and capable of providing a cell for sealing liquid crystals having high reliability without causing bleeding and oil drops.

**CONSTITUTION:** The objective resin composition for sealing liquid crystals at <1wt.% impurity concentration measured according to a solvent extraction method is obtained by blending an epoxy resin (e.g. bisphenol A type epoxy resin) with an organic acid hydrazide compound (e.g. salicylic acid hydrazide), a rubber (e.g. an acrylic acid ester-based rubber), a filler (e.g. calcium carbonate) and a solvent (e.g. n-heptane) as principal components. This resin composition is applied onto a substrate for a cell and predried. An adherend material for the cell is then applied thereto and thermoset to afford the objective cell for sealing the liquid crystals having reliability even when the prepared liquid crystal panel is exposed to severe environment without causing the bleeding or oil drops.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The resin constituent for the liquid crystal closures which is a resin constituent for the liquid crystal closures which uses an epoxy resin, an organic-acid hydrazide compound, rubber, a bulking agent, and a solvent as a principal component, and is characterized by the high impurity concentration by the solvent extraction process being less than 1 % of the weight among this resin constituent.

[Claim 2] The manufacture approach of the cel for the liquid crystal closures which assigns the adherend for cels and is characterized by carrying out heat hardening after it applies this resin constituent on the base material for cels and it carries out predrying.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the cel for the liquid crystal closures using the resin constituent suitable for the closure of the liquid crystal display of which the high dependability which can be used by diversification of a display function in recent years and the severe operating environment is required, and this resin constituent.

[0002]

[Description of the Prior Art] In recent years, the development of the so-called flat panel (a liquid crystal panel is called hereafter.) using the liquid crystal display focusing on the industry of an electron and an electrical part, or a precision instrument is prosperous. Although many liquid crystal panels to articles of consumption, such as a desktop computer, a wrist watch, and a toy, have been used at the beginning, recently, the field of the invention has spread to a personal computer, the instruments for automobiles, color television, an industrial device, etc. In connection with it, a component part for liquid crystal panels, an ingredient, etc. which can respond to diversification of a display function and a severe operating environment are demanded. Conventionally, about the resin for the liquid crystal closures which is one of the components of a liquid crystal panel, a 1 liquid system heating hardenability epoxy resin and ultraviolet-rays hardenability resin are used. For example, the 1 liquid system heating hardenability epoxy resin is indicated by JP,57-137317,A and JP,59-157330,A. However, these ingredients were insufficient in the high-reliability for corresponding to diversification of the latest display function, and a severe operating environment, and it was dissatisfied also about the problem of the blot in inspection of the finished product which enclosed liquid crystal further, or an oil droplet. That is, in inspection of the finished product which has high-reliability with a sealing agent with small (a sealing layer is thin) the finest possible seal width and a cel gap, and moreover enclosed liquid crystal by contraction of a cel gap, the shift to a large-sized panel, etc., the sealing agent with few blots and oil droplets is demanded. The purpose of this invention is offering the resin constituent for the liquid crystal closures with high-reliability with the applicability in the large application range so that it may meet the request of a raise in reliance of such a liquid crystal display object.

[0003]

[Means for Solving the Problem] By using specific rubber together to the conventional epoxy resin system sealing agent, and controlling the impurity in this resin constituent below in a certain fixed amount further, the resin constituent for the liquid crystal closures with which are satisfied of the above-mentioned request was obtained, and this invention persons completed a header and this invention for the ability of the highly reliable cel for the liquid crystal closures to be manufactured using this resin constituent. That is, it is the resin constituent for the liquid crystal closures which uses (1) epoxy resin, an organic-acid hydrazide compound, rubber, a bulking agent, and a solvent as a principal component, and the high impurity concentration by the solvent extraction process is less than 1 % of the weight among this resin constituent, and after this invention applies (2) this resin constituent on the base material for cels and carries out predrying, it is the manufacture approach of the cel for the liquid crystal

closures characterize by assign and carry out heat hardening of the adherend for cels.

[0004] First, the resin constituent of this invention is explained concretely. The epoxy resin used for this invention is a compound which has two or more epoxy groups in a molecule. For example, (1) \*\*. bisphenol A, Bisphenol F, \*\*. phenol, or novolak resin of cresol and formaldehyde that carried out addition condensation, Tetra-hydroxyphenyl methane and a hydroxy compound like resorcinol, \*\*. Carboxy compounds, such as polyhydric alcohol, such as amine compounds, such as diamino diphenylmethane, an aniline, and xylylene diamine, \*\*. glycerol, and pentaerythritol, \*\*. phthalic acid, and a hexa hydro phthalic acid etc., The resin which halogenated this polycondensation resin in the polycondensation resin list with methyl epihalohydrin, such as epihalohydrin, such as epichlorohydrin and epibromohydrin, and methyl epichlorohydrin, (2) Epoxidation fatty acids, such as epoxidized soybean oil, and the derivative of those, (3) epoxidation polybutadiene, Epoxidation diene polymers, such as epoxidation polyisoprene, (4) 3, 4-epoxy -6 - Methylcyclohexyl methyl, 3, 4-epoxy -6 - Methylcyclohexane carbonate and screw (2 3 - epoxy cyclopentyl) They are aliphatic series epoxy resins, such as the ether, etc. these -- one kind -- or two or more kinds may be used. Also in these, the group of the above (1) and also the thing of division \*\* - \*\* are good as an especially suitable thing.

[0005] the average molecular weight of the epoxy resin used for this invention -- usually -- 300-1500 -- desirable -- It is 400-1000. This average molecular weight Less than by 300, adhesion with the ingredient which constitutes the cel will be bad, and sufficient physical and chemical stability will not be obtained, and especially thermal resistance will fall. Moreover, this 1500 When are exceeded and the base material for cels and the adherend for cels after predrying are accumulated on the adhesion side after predrying since adhesion is scarce, it has defects, like the workability at the time of shifting by the external impact, vibration, etc. or applying a sealing agent falls. In addition, average molecular weight here is number average molecular weight, and when the epoxy resin to be used is two or more sorts, it means those averaged number average molecular weight. In this invention, as an organic-acid hydrazide compound used as a curing agent of an epoxy resin Monobasic-acid hydrazide compounds, such as salicylic acid hydrazide, p-oxy-benzoic-acid hydrazide, and phenylamino propionic-acid hydrazide, And succinic-acid dihydrazide, adipic-acid dihydrazide, isophthalic acid dihydrazide, They are one kind or two kinds or more of things chosen from dibasic-acid dihydrazide compounds, such as dodecanoic acid dihydrazide, sebacic acid dihydrazide, thiodipropionic acid dihydrazide, flange carboxylic-acid dihydrazide, and cyclohexane-carboxylic-acid dihydrazide. The dibasic-acid dihydrazide compound is suitable especially in these.

[0006] When these organic-acid hydrazide compounds act as a curing agent of an epoxy resin and it mixes with an epoxy resin, the storage stability in a room temperature is good, and mixture can be used as a 1 liquid type epoxy resin. Moreover, an organic-acid hydrazide compound has hardening to which very advanced thermal resistance, cold energy-proof nature, and a water resisting property are made to give, and does not have generating of the harmful matter electrically, either, while it starts a hardening reaction at low temperature comparatively compared with the curing agent used for other 1 liquid type epoxy resin adhesives, for example, a dicyandiamide, its derivative, boron-trifluoride-amine complex, etc.

[0007] as the amount of the curing agent of an epoxy resin -- per one mol of epoxy groups of an epoxy resin -- usual 0.05-0.50 mols -- desirable -- The organic-acid hydrazide compound which has a 0.15-0.35-mol hydrazide radical is used. This amount 0.05 Less than [ mol ], while producing the activity-defect in which a long duration important point is carried out to hardening, defects, like the fall of the bond strength of a sealing agent and the electric insulation of the cel manufactured become inadequate are produced. Moreover, this amount 0.50 If a mol is exceeded, the problem that moisture resistance especially falls will be produced. In addition, it is desirable to knead the organic-acid hydrazide compound which is generally a solid-state with 3 rolls etc., homogeneity and in order to make it distribute finely, and to mix.

[0008] As long as it is rubber which the rubber particle is distributing in a resin layer and which can take the so-called sea / island structure after an epoxy resin system sealing agent hardens the rubber used for this invention, any are sufficient as it. As this rubber, although an acrylic ester system, a silicone system,

a conjugated diene system, an olefin system, a polyester system, an urethane system, etc. are mentioned for example, the polymer of an acrylic ester system, a silicone system, and a conjugated diene system is desirable especially, and an acrylic ester system and a silicone system are more more desirable still. These may be used independently or may be used together.

[0009] After distributing to an epoxy resin or dissolving in an epoxy resin as the approach of distribution of a rubber particle, you may make it deposit at the time of hardening. The method of making a rubber particle generate under existence of a graft copolymer with an epoxy resin and a graft copolymer with an epoxy resin is also good. The approach of being easy to control the particle size of rubber, such as an approach of making a rubber particle generating, by the bottom of existence of a graft copolymer with an epoxy resin and a graft copolymer with an epoxy resin preferably is good. These approaches are approaches which have the interaction in rubber and a resin interface and are distributed to stability. If it does not have an interaction in rubber and a resin interface, it will be easy to condense after hardening and will be hard to hold advanced dependability. Moreover, when rubber is constructing the bridge moderately, a rubber particle cannot carry out deformation etc. easily due to the stress by hardening, and it is much more good.

[0010] Although there are some which are indicated by the approach using the rubber particle obtained by drying a core shell mold emulsion as acrylic ester system rubber and JP,55-16053,A, or JP,55-21432,A, the latter thing is desirable, considering the distributed approach or the viscosity after distribution. The approach using a silicone rubber particle as silicone system rubber, the approach currently indicated by JP,60-72957,A, Introduce a double bond into the approach and epoxy resin which are indicated by JP,3-170523,A, make the hydrogen radical content silicone in which the double bond and reaction are possible react, and a graft object is generated. The approach of carrying out the polymerization of the silicone rubber monomer under existence of a graft object, the approach of introducing a double bond into an epoxy resin, making the vinyl group content silicone monomer in which a polymerization is possible react to it, and generating a graft object, There is the approach of carrying out the polymerization of the silicone rubber monomer under existence of this graft object etc. It is easy to control the rubber particle which the approach of generating the rubber particle after generation is good, and generates a graft object and a graft object by these approaches preferably, without using a silicone rubber particle, and there are few rises of the viscosity after distribution, and a good result is brought to the printing nature of a sealing agent. These approaches are approaches which have the interaction in rubber and a resin interface and are distributed to stability. If it does not have an interaction in rubber and a resin interface, it will be easy to condense after hardening and will be hard to hold advanced dependability. Moreover, since rubber is [ that a rubber particle cannot carry out deformation etc. easily due to the stress by hardening ] good in addition when it is gelled moderately, in addition, it is good to choose the monomers to be used. What is necessary is to be able to say the same thing also with acrylic ester system rubber, to use the monomer which has a glycidyl group on a graft object, or just to devise carrying out optimum dose use of the monomer which has the vinyl group of many \*\* etc.

[0011] as conjugated diene system rubber -- monomers, such as 1,3-butadiene, 1,3-pentadiene, an isoprene, 1, 3-hexadiene, and a chloroprene, -- a polymerization -- or it copolymerizes, and it can manufacture and a commercial item can be used. Especially the copolymer of the butadiene and acrylonitrile which have a carboxyl group at the end, the copolymer of the butadiene and acrylonitrile which have an amino group at the end, etc. melt into an epoxy resin, and tend [ comparatively ] to control a rubber particle by the type by which rubber deposits at the time of hardening. However, control of particle size may become inadequate on the engine performance [ it is difficult and / the aforementioned two-way-type method (acrylic ester system rubber and silicone system rubber) ].

[0012] as the particle size of the rubber used for this invention -- mean particle diameter -- usually -- 0.01-5 micrometers desirable -- 0.01-2 micrometers The rubber which can take the so-called sea / island structure currently distributed by the particle is good. the above [ mean particle diameter ] -- being out of range -- if -- this invention -- high-reliability is not acquired but there is performance degradation. Moreover, the amount of the rubber used is the inside of this resin constituent, and usual. It is 2 - 20 %

of the weight preferably 0.5 to 25% of the weight. This amount At less than 0.5 % of the weight, if the bond strength at the time of a humid ambient atmosphere is not enough and exceeds 25 % of the weight, the viscosity of a sealing agent rises, workability, such as the printing nature of a sealing agent, will fall, or trouble, like adhesion becomes scarce will come out to the adhesion side after predrying.

[0013] As a bulking agent used by this invention, carbonates, such as (1) calcium carbonate and a magnesium carbonate, Sulfates, such as a barium sulfate and magnesium sulfate, an aluminum silicate, Silicates, such as zirconium silicate, ferrous oxide, titanium oxide, an aluminum oxide (alumina), Oxide, such as a zinc oxide and a silicon dioxide, potassium titanate, a kaolin, Inorganic bulking agents, such as talc, asbestos powder, quartz powder, a mica, and a glass fiber, And (2) polyethylene powder, polypropylene powder, polyester powder, There are organic bulking agents, such as polyvinyl chloride powder, polystyrene powder, polyvinyl acetate powder, a polyethylene-vinyl acetate copolymer, polymethacrylate powder, polyurethane powder, urea-resin powder, phenol resin powder, benzoguanamine resin powder, and epoxy resin powder. Generally the addition of these bulking agents is an epoxy resin 100, although it changes with the presentation of the sealing agent used for this invention, especially the classes of the bulking agent itself a lot. It is 1-100 to the weight section. The range of the weight section is desirable. Under in 1 weight section, this amount has bad spreading workability and tends to produce defects, like the holdout of the applied pattern is also inferior.

Moreover, this amount Trouble tends to be caused to spreading by screen-stencil etc. if the 100 weight sections are exceeded. In addition, it is desirable to use it with 3 rolls etc. in mixing of a bulking agent for clogging prevention of the screen at the time of screen-stencil etc., kneading and making it detailed.

[0014] In this invention, as for a sealing agent, it is desirable to contain a solvent, and its thing of the boiling point 70 - 250 \*\* is desirable as a solvent. Specifically, it is n. - A heptane, n - An octane, n - Deccan, a cyclohexane, Benzene, toluene, a xylene, ethylbenzene, amyl benzene, Hydrocarbons, such as naphthalene and a pinene; A carbon tetrachloride, an ethylene chloride, 1,1,1-trichloroethane, 1, 1, 1, 2-tetrachloroethylene, hexa chloroethylene, a trichloroethylene, Tetrachloroethylene, 1,2,3-trichloropropane, a butyl chloride, Chlorination amyl, chlorination -2 - Ethylhexyl one, an ethylene bromide, tetrabromo ethane, Halogenated hydrocarbon, such as a chlorobenzene, 1,2,4-trichlorobenzene, and a bromobenzene; Ethanol, Isopropanol, n - Amyl alcohol, fusel oil, n - Hexanol, Methyl amyl alcohol, 2-ethyl butanol, n - Heptanol, n - An octanol, n - Decanol, a cyclohexanol, benzyl alcohol, Alcohols, such as furfuryl alcohol; n-butyl ether, n - Hexyl ether, The ether and acetals, such as ethyl phenyl ether, 1,4-dioxane, a trioxane, and a diethyl acetal; Formic-acid propyl, Formic-acid isopropyl, ethyl acetate, acetic acid - n - Butyl, benzyl acetate, Ester, such as isoamyl butyrate, ethyl lactate, methyl benzoate, and oxalic acid diethyl; Ethylene glycol, Methyl cellosolve, methyl-cellosolve acetate, a cellosolve acetate, Dibutyl cellosolve, methyl carbitol, carbitol acetate, Polyhydric alcohol, the derivatives of those, such as butyl carbitol, propylene glycol, and hexylene glycol; sulfur-containing solvents, such as dimethyl sulfoxide, N, N - Nitrogen-containing solvents, such as dimethylformamide, etc. are mentioned. The number of these solvents may be one, and even if it uses it combining two or more kinds, they do not interfere.

[0015] The boiling point of the solvent used by this invention During storage of a sealing agent or a sealing agent spreading activity, a solvent volatilizes, the viscosity of a sealing agent goes up under by 70 \*\*, and there is an inclination to worsen workability. Moreover, the boiling point of a solvent If 250 degrees C is exceeded, while a predrying process will take long duration, there is a danger of a solvent remaining and reducing the engine performance of the liquid crystal in a cel into the applied sealing agent, and an adhesive property may be insufficient. The reason for adding a solvent by this invention is for giving a fluidity to a sealing agent and giving moderate spreading nature. Therefore, generally the addition of a solvent is an epoxy resin 100, although to adjust so that these conditions may be fulfilled is required. The range of 0 - 70 weight section is suitable to the weight section.

[0016] In this invention, adding other well-known curing agents if needed will not interfere at all, if it is the range which does not spoil the effectiveness of this invention. As the curing agent, aromatic amine, fatty amine, an acid anhydride, a boron-trifluoride compound, a dicyandiamide and its derivative, imidazole derivatives and its salts, diaminomaleonitrile and its derivative, nylon, and a urea derivative

are mentioned. Furthermore, various additives, such as surface treatment agents, such as a hardening accelerator, a silane coupling agent, and a titanate system coupling agent, and a pigment, a plasticizer, a leveling agent, a reactant diluent, and a defoaming agent, can also be used in the range which does not spoil the effectiveness of this invention if needed. As the sealing agent which contained the solvent from the standpoint used for the cel for the liquid crystal closures further at the beginning although the sealing agent used for this invention comes to contain the various components explained above With 25 \*\* It is desirable not to have a fluidity, even if the paint film applied to 1mm thickness as a sealing agent which has the viscosity of 100-1500poise, and contained the solvent is perpendicular in a paint film side after volatilization of a solvent.

[0017] Next, the impurity in this invention is an impurity contained in this resin constituent, and what is after this hardening termination and does not become a part in a hardening constituent, and the thing to which the solvent extraction of the molecular weight is easy to be carried out small are said. This impurity is matter which begins to melt into liquid crystal, or is extracted, and causes a blot and an oil droplet, after enclosing liquid crystal. Although the degree which this matter produces changes with classes of liquid crystal to be used, it is called for by the following quantitative-analysis method as high impurity concentration. This value is well in agreement with the result of inspection of the finished product which enclosed liquid crystal. That is, when this impurity was less than 1 % of the weight, it became clear in inspection of a finished product that it is good.

[0018] In this invention, in order to stop the concentration of this impurity to less than 1% of the weight, there are various approaches. For example, the purity of the constituent of this resin constituent is raised, a partially aromatic solvent extracts beforehand the constituent of the approach of devising so that the concentration of an impurity may become less than 1% of the weight, and this resin constituent, any are sufficient as the approach of reducing the concentration of this impurity, the approach of washing this resin constituent with the solvent which does not dissolve in itself, etc., and they should just be suppressed to less than 1% of the weight in the concentration of this impurity at any rate. The concentration of an impurity is that what is necessary is just less than 1 % of the weight. 0.5 or less % of the weight is good.

[0019] In addition, in this invention, the quantitative-analysis method of an impurity is as follows. It is the hardened material of this resin constituent 100 It grinds to the fines of mesh pass, 1g of these grinding articles is strong-stirred in partially aromatic solvent (n-hexane / ethyl-acetate =9/1 pile quantitative ratio) 100 g, and an impurity is extracted. A gas chromatograph analyzes the impurity in this extract, and it is  $x(\text{total amount of the total amount/peak area of the peak area of an impurity}) 100$ . It computes assuming that it is the high impurity concentration in this extract, it is converted into per this resin constituent, and it considers as high impurity concentration (% of the weight).

[0020] Furthermore, the typical manufacture approach of the cel for the liquid crystal closures of this invention is explained concretely. The sealing agent which mixed the bulking agent (spacer) for obtaining a desired gap to the sealing agent which uses a solvent as a principal component by request at the aforementioned epoxy resin, an organic-acid hydrazide compound, rubber, and a bulking agent list is applied so that thickness suitable on the base material for cels and usual may become about 2 to 3 times [ of request thickness ] thickness mainly by screen-stencil, and it carries out predrying with a drying furnace etc. Then, heat hardening is carried out with the means of a drying furnace, a hot plate, a heater block, an infrared heater, etc., putting the adherend for cels and pressurizing by collet pressurization, a vacuum pin, etc.

[0021] In order to give the thing and transparent electrode which carried out surface treatment of minerals ingredients, such as (1) glass, and the (2) above-mentioned minerals ingredients by surface treatment agents, such as a silane coupling agent, the orientation film, etc., as for the base material for cels used by this invention, what carried out surface treatment is typical. Moreover, as for the adherend for cels used by this invention, the (1 [ same ]) and (2) as said base material for cels are typical, and you may have the same ingredient and same configuration as said base material for cels, and may differ. [ same ]

[0022] With predrying in this invention, the solvent contained in a sealing agent is volatilized enough,

and it means maintaining a moderate fluidity so that a sealing agent layer may get used to a part for jointing of an adherend, in case heat hardening of the adherend for cels is put and carried out after this, and volatilizing the minute amount moisture which remains in a sealing agent in a list. When it is usually the range of 5 minutes - 6 hours at 130 degrees C from a room temperature and productivity and economical efficiency are taken into consideration among an air current as desiccation conditions, it is 20-120 at 60 - 110 \*\*. The range of a part is desirable.

[0023] The heat hardening in this invention means making the hardening reaction of an epoxy resin and an organic-acid hydrazide compound perform enough, and carrying out the glued connection of the base material for cels, and the adherend for cels with a sealing agent among a sealing agent component. as hardening conditions -- the inside of an air current -- usually -- 130 - 220 \*\* -- 5-180 a part -- it is -- desirable -- 150 - 200 \*\* 20-120 a part -- the range is suitable.

[0024]

[Example] Hereafter, a synthetic example, an example, and the example of a comparison explain this invention to a detail. The "section" and "%" are weight criteria below.

The following were compounded as a synthetic example 1 rubber component. Bisphenol F system epoxy resin 600 made from Bisphenol F and epichlorohydrin (Epiclone 830 S; a trade name, Dainippon Ink make) The section, acrylic acid 12 Epoxy resin which introduced acrylic-acid residue by adding the section and the triethylamine 1 section, carrying out a temperature up and making it react to 110 \*\* for 5 hours The 613 sections were manufactured. Next, it is butyl acrylate to this. The 350 sections, glycidyl methacrylate 20 The section, the divinylbenzene 1 section, the azobis dimethylvaleronitrile 1 section, and the azobisisobutyronitril 2 section were added, the polymerization was carried out at 90 more degrees C by 70 degrees C for 1 hour for 3 hours, and the graft polymer of an epoxy resin and an acrylic ester system was manufactured. This polymer (A-1) is the mean particle diameter of 0.05 micrometers. It has the so-called sea / island structure, and they are weight-per-epoxy-equivalent 305 g/eq and 37.9% of rubber contents.

[0025] Epoxy resin which operated it like the example 1 of synthetic example 2 composition, and introduced acrylic-acid residue The 613 sections were manufactured. Next, the hydroxyethyl acrylate 5 section, the butyl acrylate 10 section, and the azobisisobutyronitril 1 section were added to this, the polymerization was carried out at 90 more degrees C by 70 degrees C for 1 hour for 3 hours, and the graft polymer of an epoxy resin and an acrylic ester system was manufactured. Furthermore, the silicone intermediate-product (DC-3037; trade name, Toray Industries silicone company make) 70 section which has a methoxy group, and the dibutyltin dilaurate 0.3 section were added into the molecule, and it reacted to this for 1 hour. The methanol generated under reduced pressure of 20Torr was distilled off for 30 minutes in the second half of a reaction. Thus, the graft object of the conversion resin of an epoxy resin and a silicone compound was manufactured. To this, it is 1:1 mixed liquor of KE-1204A (a trade name, Shin-Etsu Chemical Co., Ltd. make) and KE-1204B (a trade name, Shin-Etsu Chemical Co., Ltd. make) as room-temperature-setting mold silicone rubber. It was made to react for 2 hours, adding and strong-stirring the 300 sections, and the epoxy resin which silicone rubber distributed was manufactured. This polymer (A-2) is the mean particle diameter of 1.5 micrometers. It has the so-called sea / island structure, and they are weight-per-epoxy-equivalent 308 g/eq and 30.0% of rubber contents.

[0026] Epoxy resin which operated it like the example 1 of synthetic example 3 composition, and introduced acrylic-acid residue The 613 sections were manufactured. Next, the radical reaction nature silicone oil (X-22-5002; trade name, Shin-Etsu Chemical Co., Ltd. make) 50 section and the azobisisobutyronitril 1 section were added to this, the polymerization was carried out at 90 more degrees C by 70 degrees C for 1 hour for 3 hours, and the graft polymer of an epoxy resin and a silicone compound was manufactured. Furthermore, it is 1:1 mixed liquor of KE-1204A (a trade name, Shin-Etsu Chemical Co., Ltd. make) and KE-1204B (a trade name, Shin-Etsu Chemical Co., Ltd. make) as room-temperature-setting mold silicone rubber to this. It was made to react for 2 hours, adding and strong-stirring the 300 sections, and the epoxy resin which silicone rubber distributed was manufactured. This polymer (A-3) is mean particle diameter 0.5. mum It has the so-called sea / island structure, and they are weight-per-epoxy-equivalent 297 g/eq and 31.1% of rubber contents.



[0027] the inside of the various components of one to example 3 table 1 (Table 1), epoxy resin A, epoxy resin B, a polymer (A-1) - a polymer (A-3), and a curing agent (adipic-acid dihydrazide) -- to the one section, the partially aromatic solvent (n-hexane / ethyl-acetate =9/1 pile quantitative ratio) 10 section came out comparatively, and it mixed, and in ordinary temperature, it stirs for 3 or so hours, solvent extraction was carried out, and removal desiccation of the solvent was carried out, respectively. Then, it mixes with mixers, such as a Henschel mixer, the Dalton mixer, and a ball mill, at a rate as shown in Table 1 (Table 1), and particle size four components and other components which were obtained by the above-mentioned extract operation with 3 rolls 10 mum It kneads until it becomes below (it is 5 micrometers preferably following). Kneading object The 100 sections and the spacer (5 micrometer [ of diameters ], milled fiber) 1.5 section are enough mixed at a room temperature. It left liquid crystal enclosure opening to the 1st glass substrate (with a transparent electrode), and the obtained resin constituent for the liquid crystal closures was screen-stenciled to it (325 mesh). Next, predrying was carried out for 20 minutes at 90 degrees C, and it cooled at the room temperature. With furthermore, 150 \*\* after sticking the 2nd glass substrate (with a transparent electrode) to the obtained glass substrate by pressure with lamination and a butterfly clip 60 Book hardening between parts was carried out. About the empty panel obtained here, it evaluated as follows and the result was shown in Table 3 (Table 3). On the other hand, biphenyl mold liquid crystal was enclosed from liquid crystal enclosure opening, enclosure opening was stopped in the obtained empty panel, by SUTORAKUTO bond ES-280 (a trade name, Mitsui Toatsu Chemicals, Inc. make), and the liquid crystal panel was produced. About the obtained liquid crystal panel, it evaluates as follows and the result is shown in Table 3 (Table 3).

[0028] Further, it mixed to this mixture 1 section at a rate of the partially aromatic solvent (n-hexane / ethyl-acetate =9/1 pile quantitative ratio) 10 section, and in ordinary temperature, it stirs for 3 or so hours, solvent extraction was carried out [ the component only except a solvent (methyl carbitol) is mixed at a predetermined rate in the various components of four to example 6 table 1 (Table 1) ], and removal desiccation of the solvent was carried out. Then, it mixes with a mixer at a rate as shown in Table 1 (Table 1), and particle size the mixture and the solvent (methyl carbitol) which were obtained by the above-mentioned extract operation with 3 rolls 10 mum It kneads until it becomes below (it is 5 micrometers preferably following). After this, it was operated completely like examples 1-3, and the empty panel and the liquid crystal panel were obtained. About what was obtained, it is similarly estimated as examples 1-3, and the result is shown in Table 3 (Table 3).

[0029] Without performing extract operation in one to example of comparison 4 examples 1-6, various components are mixed with a mixer at a rate as shown in Table 2 (Table 2), and particle size with 3 rolls 10 mum It kneads until it becomes below (it is 5 micrometers preferably following). After this, it was operated completely like examples 1-6, and the empty panel and the liquid crystal panel were obtained. About what was obtained, it is similarly estimated as examples 1-6, and the result is shown in Table 3 (Table 3). In addition, evaluation of the empty panel and liquid crystal panel which were produced was performed as follows.

- Workability; the engine performance to printing nature until it produces an empty panel, predrying, lamination, and this hardening was named generically, and it judged synthetically.

evaluation x ... problematic -- \*\* ... some -- problematic -- O ... fitness O ... outstanding - pattern shapeability; -- in the empty panel, the existence of a blot of the transparent matter from a resin hardened material and the quality of a pattern configuration were observed under the microscope (scale factor 200).

evaluation x ... the transparence matter -- many pattern configuration turbulence \*\*s ... the transparence matter and \*\* -- many pattern configurations and \*\*\*\*\*O ... transparence matter nothing and pattern configuration fitness [0030] - Electrical property; liquid crystal panel By the environment of 80 \*\*x95% RH 2000 The specific resistance between the terminals after time amount neglect was measured, and long-term dependability was judged by distribution of rate of change.

Evaluation x [ ... The dependability fitness and adhesion; liquid crystal panel of the long period of time / fluctuation / in smallness / After 2000 hour neglect and a knife were inserted in the environment of RH from enclosure opening 80 \*\*x95%, and the exfoliation situation of a panel was observed ] ... \*\* with

fluctuation lacking in long-term large dependability ... O with fluctuation a little lacking in dependability long-term in inside

Evaluation x [ ... It did not exfoliate but the blot which operates and cannot sense a - blot; liquid crystal panel under a microscope in the poor orientation was investigated. ] ... \*\* which exfoliates simply ...

Exfoliation, \*\*\*\*, O

Evaluation x [ ... Poor orientation observed the good - oil droplet; liquid crystal panel under the microscope (scale factor 200) by smallness, and it investigated the number of an oil droplet. ] ... \*\* with poor large orientation ... O whose poor orientation is whenever [ middle ]

Evaluation x [ ... [0031] with an oil droplet good at smallness ] ... There are many oil droplets. \*\* ... O whose oil droplet is whenever [ middle ]

[Table 1]

表 1

組成単位； 部

|               | 実 施 例 |     |     |     |     |     |
|---------------|-------|-----|-----|-----|-----|-----|
|               | 1     | 2   | 3   | 4   | 5   | 6   |
| エポキシ樹脂A (* 1) | 280   | 280 | 280 | 280 | 280 | 280 |
| エポキシ樹脂B (* 2) | 220   | 220 | 220 | 220 | 220 | 220 |
| A-1           | 150   | —   | —   | 150 | —   | —   |
| A-2           | —     | 150 | —   | —   | 150 | —   |
| A-3           | —     | —   | 150 | —   | —   | 150 |
| アジピン酸ジヒドラジド   | 50    | 50  | 50  | 50  | 50  | 50  |
| アエロジル         | 50    | 50  | 50  | 50  | 50  | 50  |
| アルミナ          | 150   | 150 | 150 | 150 | 150 | 150 |
| メチルカルビトール     | 100   | 100 | 100 | 100 | 100 | 100 |
| 不純物濃度 (%)     | 0.1   | 0.3 | 0.2 | 0.7 | 0.9 | 0.8 |

\* 1; bisphenol A/Epichlorohydrin polycondensation mold epoxy resin molecular weight 900 Weight per epoxy equivalent 450 g/eq\*2; bisphenol F/Epichlorohydrin polycondensation mold epoxy resin molecular weight 540 Weight per epoxy equivalent 200 g/eq [0032]

[Table 2]

表 2

組成単位； 部

|               | 比 較 例 |     |     |     |
|---------------|-------|-----|-----|-----|
|               | 1     | 2   | 3   | 4   |
| エポキシ樹脂A (* 1) | 280   | 280 | 280 | 370 |
| エポキシ樹脂B (* 2) | 220   | 220 | 220 | 280 |
| A-1           | 150   | —   | —   | —   |
| A-2           | —     | 150 | —   | —   |
| A-3           | —     | —   | 150 | —   |
| アジピン酸ジヒドラジド   | 50    | 50  | 50  | 50  |
| アエロジル         | 50    | 50  | 50  | 50  |
| アルミナ          | 150   | 150 | 150 | 150 |
| メチルカルビトール     | 100   | 100 | 100 | 100 |
| 不純物濃度 (%)     | 1.5   | 2.1 | 1.9 | 1.0 |

[0033]

[Table 3]

表 2

組成単位； 部

|               | 比 較 例 |     |     |     |
|---------------|-------|-----|-----|-----|
|               | 1     | 2   | 3   | 4   |
| エポキシ樹脂A (* 1) | 280   | 280 | 280 | 370 |
| エポキシ樹脂B (* 2) | 220   | 220 | 220 | 280 |
| A-1           | 150   | —   | —   | —   |
| A-2           | —     | 150 | —   | —   |
| A-3           | —     | —   | 150 | —   |
| アジピン酸ジヒドラジド   | 50    | 50  | 50  | 50  |
| アエロジル         | 50    | 50  | 50  | 50  |
| アルミナ          | 150   | 150 | 150 | 150 |
| メチルカルビトール     | 100   | 100 | 100 | 100 |
| 不純物濃度 (%)     | 1.5   | 2.1 | 1.9 | 1.0 |

[0033]

[Table 3]